

SUBCONTRACT TITLE: **FABRICATION AND PHYSICS OF CDTE DEVICES BY SPUTTERING**

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SUBMITTED TO: **Ken Zweibel**
National Renewable Energy Laboratory

PRINCIPAL INVESTIGATORS: A.D. Compaan (P.I.), V. G. Karpov (co-P.I.),
R.W. Collins (co-P.I.) and D. Giolando (co-I)
University of Toledo,
2801 W Bancroft,
Toledo, OH 43606

This progress report covers the third quarter of Phase 1 for the period September 1, 2005, through November 30, 2005, of the above Thin Film Photovoltaic Partnership Program subcontract. During this quarter we worked on thin CdTe solar cell limitations, spatial and temporal variations in electronic transport through a CdTe-based Schottky barrier, device physics modeling, and ellipsometric diagnostics. In this report we highlight our recent results on the distribution of copper in sputtered CdTe solar cells (task 1.3.4) and recently discovered reversible piezo-effect in CdTe/CdS solar cells consistent with the piezo parameters of CdS, which strongly supports our MIS device model (task 1.2.1).

Copper distribution in Cu/Au contacted, sputtered CdTe Cells (Task 1.3.4 Extended X-ray Absorption Fine Structure)

Concurrent with our studies of x-ray absorption fine structure at the Argonne Advanced Photon Source (APS), we have used x-ray fluorescence intensity as a convenient method to determine the total amount of copper in a solar cell structure. X-ray beam excitation is advantageous over electron beam excitation, for these structures, since a ~ 10 keV x-ray beam penetrates completely through CdTe layers up to $10\text{ }\mu\text{m}$ thick. By taking advantage of the intense (*peak brilliance at 6.5keV: 9.6×10^{18} ph/sec/mrad²/mm²/0.1% bw*) and stable x-ray beam of the APS and the high purity Ge multi-element detector of Materials Research Collaborative Access Team (MRCAT) beamline, we are able to investigate low-level Cu concentrations in our CdTe cells (typically $\sim 0.3\%$, averaged through the structure). Furthermore, we have used a lift-off or peel-off process to separate the

Cu/Au back contact and independently measure the amount of Cu in the contact and in the residual solar-cell structure.

UT CdTe based solar cells are usually contacted with 35Å Cu and 200Å Au on the surface of CdCl₂ treated, sputtered CdTe/CdS/TCO/glass structures. No water rinse or acid etching is used after the Cl treatment and the depositions of the Cu and Au layers are completed without vacuum break. A 45-minute heat treatment at 150 °C in air is employed to diffuse some of the Cu into the cells. SIMS studies of similar sputtered cells and cells fabricated with other contact processes typically show that Cu produces some doping throughout the CdTe and a heavily-doped layer near the back contact. In this study we combined the fluorescence signal with the EXAFS spectra and the peel-off process to examine the location of the Cu and its lattice environment. Furthermore, we have recontacted the cells after the contact peel-off process to determine whether additional Cu is required to obtain good performance.

We prepared complete cells with 0.13 μm CdS and 2.3 μm CdTe on TEC-7 glass, standard CdCl₂ treatment and then 35Å Cu / 200Å Au followed with 45 minutes diffusion. These samples were prepared for Cu K-edge EXAFS studies on the CdTe film in complete cells, in which the Au layers are usually peeled off by epoxy (Figure 1a). The peel-off process can readily be adjusted to separate either the metal layer from the rest of the structure or the CdTe layer from the CdS layer.

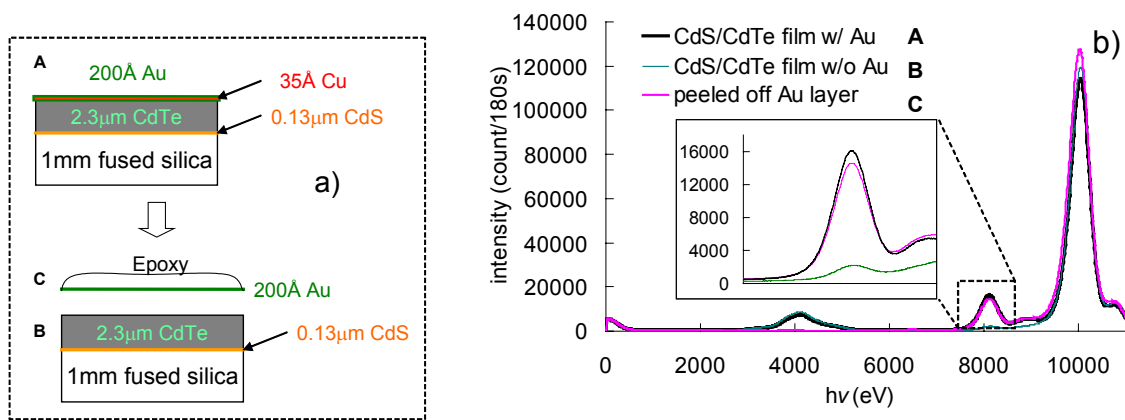


FIG. 1. a) schematic structures of the samples; b) x-ray fluorescence of CdS/CdTe film with Cu/Au metal layer (A), film without metal layer (B), and the peeled-off Cu/Au layer (C). Note: the peak at 8048 eV is Cu K α fluorescence generated by the 10 keV x-ray beam.

We have used the x-ray fluorescence intensity excited at 10 keV, just above the Cu – K-absorption edge, to obtain maximum sensitivity to the Cu. We found the amount of Cu in the remaining structure of CdTe/CdS/TCO/glass to be much lower than in the peeled-off metal layers. As shown in Figure 1, the Cu K α intensity of the remaining structure (sample B) is 9.5% of the one of complete cell (sample A), while the intensity of the peeled off metal layer (sample C) on epoxy is 89.5% of that of the complete cell (sample A). Thus, ~90% of the evaporated Cu remains in the Cu/Au contact structure.

Our EXAFS data on complete solar-cell structures indicates a strong peak arising from Cu-O bonds located at the same position -1.43Å in $\chi(R)$ spectrum as the peak of the first nearest neighbor

bond (Cu-O) in Cu_2O (Figure 2). This suggests that most of the copper in the complete cell forms a copper-oxide structure as found in our earlier work on Cu-diffused, CdCl_2 -treated CdTe films. [Xiangxin Liu, Alvin D. Compaan and Jeff Terry, 31st IEEE-PVSC Specialists Conference, 2005] We are still working on FEFF fitting to the peak at around 2\AA and 2.74\AA .

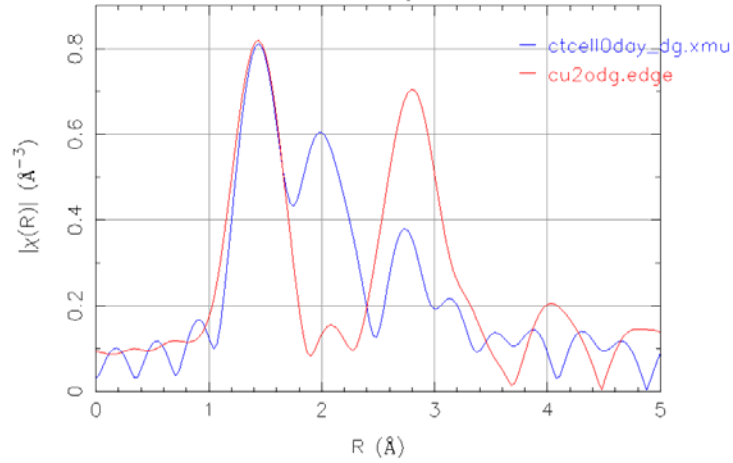


FIG. 2 The magnitudes of Fourier transformed Cu K-edge EXAFS spectra of a fresh cell (with Cu/Au contact) and Cu_2O powder. The first primary peak at 1.43\AA matches the peak arising from the first nearest neighbor peak in Cu_2O .

Thus we conclude that the equivalent of only one monolayer of Cu actually enters the CdTe layer during our standard processing. In order to test further the nature of the back contact, we used a recently assembled I-V-T system and tested a variety of cells with our standard contacts and cells that were recontacted after peeling off the original metal contact. Some of the I-V-T results of these re-contacted cells are summarized below. To investigate the role of copper at the CdTe/Au interface and that diffused into bulk or along the grain boundaries, different sets of samples were made. All the samples were made the same up to the point of the back contact evaporation. From there different back contacts were made and cell performance along with temperature dependent I-V (I-V-T) characteristics was measured.

I-V-T characterization is known to be a valuable tool for back barrier characterization. It is well known that a Schottky barrier is often formed between the absorber layer and back contact material due to the high work function of CdTe. This barrier prevents holes from contributing to the cell current and is manifest as a roll-over in the first quadrant of the I-V curve at low temperatures, as the thermal energy of the holes decreases, suppressing thermionic-field emission through the barrier.

Fig. 2 shows I-V traces of a standard UT cell with Cu/Au back contact activated by 45 minutes diffusion at $150\text{ }^\circ\text{C}$ in air. (This cell actually had a thinner than usual CdS layer which accounts for the relatively low V_{oc} and high J_{sc} . The thinner than standard CdS was confirmed by QE data showing higher blue-green sensitivity.) All eight cells on this substrate had similar but slightly lower performance than the best cell that had parameters of:

- Efficiency 10.27%
- V_{oc} 0.76 V
- J_{sc} 23 mA/cm^2
- FF 63.04

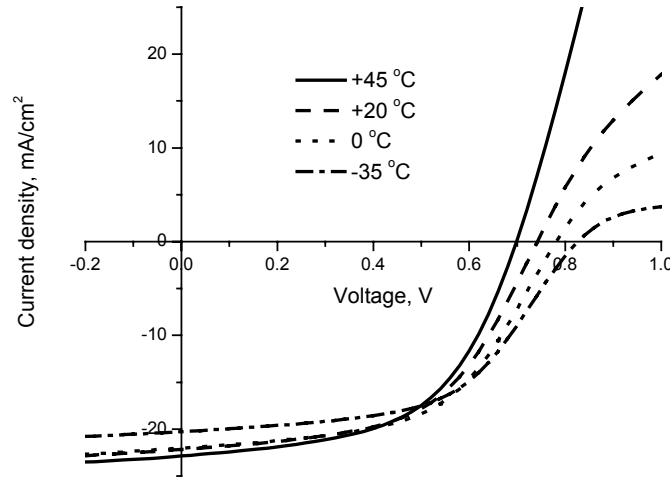


FIG. 3 I-V-T characteristics of the standard cell

We have studied the integrity of the back contact structure by using the peel-off technique and recontacting. We used three separate processes to re-contact the cells: 1) evaporation of another standard Cu/Au contact but without diffusion, 2) evaporation of the standard Cu/Au contact followed by standard diffusion, and 3) evaporation of Au alone with no diffusion.

Case #1 is expected to be likely to work since earlier Cu diffusion has already introduced Cu into the CdTe structure and thermal diffusion of the new contact may not be needed. This does not seem to be the case for the new Cu/Au contact. The efficiency is much lower. (Five of the eight contacts were very similar and three gave very low efficiency.)

- Efficiency 6.85 %
- V_{oc} 0.71 V
- J_{sc} 19.07 mA/cm²
- FF 50.72

Case #2 was chosen to explore whether a thermal treatment of the new contact would improve the results, i.e., a second diffusion of Cu might be necessary. The results show that the original efficiency was nearly recovered but with somewhat higher voltage and lower current:

- Efficiency 9.74 %
- V_{oc} 0.81 V
- J_{sc} 18.69 mA/cm²
- FF 64.25

The I-V-T data (not shown) indicate that the roll-over in the first quadrant is less, although these cells seemed to be unstable while measuring I-V-T at elevated temperature which could be an indication that an excessive amount of Cu diffused into these cells.

The last set of cells studied (case #3) seems to be free of that problem since it has been recontacted with Au (no Cu) and was not thermally treated. The performance of these cells is only slightly reduced from the original cells indicating that the additional Cu is not necessary for the

recontacting and does not increase the cell performance significantly. The best cell recontacted with gold alone has the following performance:

- Efficiency 9.06 %
- V_{oc} 0.76 V
- J_{sc} 18.82 mA/cm²
- FF 63.04

The I-V-T graphs of this cell in Fig. 4 exhibit no rollover down to almost -35 °C. This suggests that much of the copper (removed in the peel-off of the original contact and reintroduced in the recontact processes #1 and #2) is in the form of CuO_x and contributes an additional hole transport barrier as indicated already by roll-over apparent at 20 °C in Figure 3.

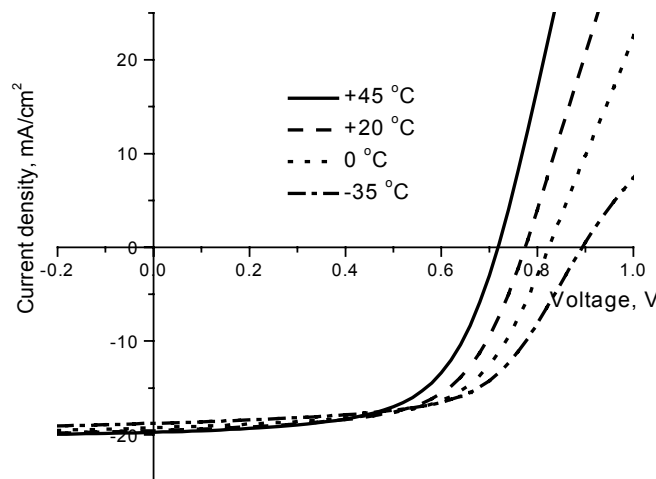


FIG. 4 I-V-T characteristics of a standard cell recontacted with Au alone

This study indicates, for sputtered CdS/CdTe cells contacted with evaporated elemental Cu and Au, that 30 Å of the 35 Å of evaporated Cu does not diffuse into the CdTe film during the back-contact formation, but is oxidized and fixed under the Au largely as Cu₂O. Since Cu is a fast diffuser in CdTe and would be expected to diffuse rapidly into the CdTe, this suggests that the Cu is oxidized quickly by the CdTe surface prepared by the vapor CdCl₂ treatment. This rapid Cu oxidation reduces the amount of elemental Cu available for diffusion into CdTe.

Piezo-effect and physics of CdS-based thin-film photovoltaics

(Task 1.2.1 MIS model of CdTe solar cells)

Two major types of polycrystalline thin-film photovoltaics (PV) based on CdTe and CuIn(Ga)Se (CI(G)S) absorber layers include a tangent thin CdS film. Empirically, this film appears irreplaceable, even though understanding of its role remains rather poor. The prevailing hypothesis is that CdS serves as a window layer buffer between the absorber and the conductive front electrode (Fig. 5 (a)). When thick ($\gtrsim 2000$ Å) it causes a substantial blue light absorption ($\hbar\omega > 2.4$ eV). This is detrimental to the device because the carrier collection from CdS is almost absent. The lack of carrier collection, while commonly recognized [1], remains puzzling. One explanation suggests an extremely high recombination rate, hardly consistent with the parameters of photoconductivity in polycrystalline CdS films [2].

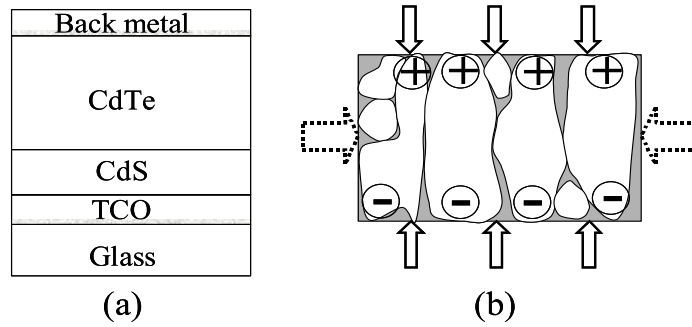


FIG. 5: (a) Sketch of CdTe/CdS PV structure; TCO stands for the transparent conductive oxide. (b) Sketch of a fragment of polycrystalline CdS layer consisting of individual (mostly columnar) grains with the + and - piezo-electric charges. Solid and dashed arrows show respectively the pressure applied in our experiments (along the c axis) and the original in-plane compressive stress.

A strong piezo-effect present in both CdS crystals [3] and polycrystalline thin films [4, 5] could be a unique factor in thin-film PV. The underlying reasoning is that in a PV device, the CdS layer is put under compression, which, through the piezo-effect, can translate into considerable voltage. It has been established, indeed, that the lattice parameter mismatch and the deposition process make the CdS layer laterally strained in the CdTe based device (characteristic strain $\epsilon \sim 0.002$; Fig. 5 (b)) [6, 7]. The possibility of piezo-electric coupling was examined for CdS/Cu₂S solar cells - without success [8] - and never addressed since then. This negative result is hard to understand in the light of simple estimates presented below.

The quantitative description is based on the piezo-electric tensor d_{ij} relating the polarization P_i to stress, i.e. $P_i = d_{ij}T_j$ (in the IEEE standard notations [9]). For the hexagonal structure of CdS, the elements of that tensor $|d_{ij}| \sim 10^{-11}$ C/N are larger in absolute value,

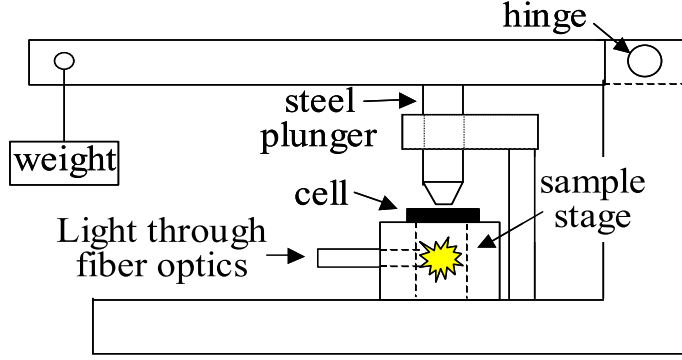


FIG. 6: Sketch of apparatus used for applying pressure perpendicular to the face of thin-film PV cell.

by at least one order of magnitude, than that of CdTe and many other semiconductors [3]. The voltage across the CdS layer can be expressed as

$$V_i = d_{ij}T_j/C_0, \quad (1)$$

where C_0 is the film capacitance per unit area.

For numerical estimates we assume the in-plane stress (perpendicular to the c axis) $T_1 = c_{11}\epsilon \sim 2 \cdot 10^8$ N/m² for the above ϵ and the elastic constant $c_{11} \approx 10^{11}$ N/m² [3]. The voltage along the c axis, i. e. across the film, is determined by $d_{31} \approx 5 \cdot 10^{-12}$ C/m² [3, 8] and geometrical capacitance $C_0 \approx 4 \cdot 10^{-4}$ F/m² (film thickness of 0.2 μ m), which yields $V_1 \sim 5V$. This 'abnormally' high voltage exceeds the CdS forbidden gap (≈ 2.4 V) and the open-circuit voltage generated by the CdTe/CdS PV ($V_{OC} \approx 0.8$ V).

Several factors could reduce the above estimated piezo-voltage. (1) Grains in the CdS film, while retaining some preferential orientation [7], can exhibit considerable structural disorder, possibly amplified by the subsequent chemical and thermal treatments [10]. (2) Charge carriers can screen the piezo-effect, introducing a reduction factor of $\sim L/l$ where L is the screening length and $l(> L)$ is the film thickness. (3) Even when the charge carrier concentration in the unstressed CdS is low, it will increase due to the band bending caused by the piezo-electric field, thus screening the field.

Assuming an order of magnitude reduction, the remnant piezo-voltage ~ 0.5 V is still comparable to the device V_{OC} and cannot be neglected. It might be due to some of masking factors (such as, CdS surface coupling with the tangent layers and ambient, surface contaminations, and shunting) that the piezo-coupling was not detected in the previous work.

We applied pressure perpendicular to the cell surface by means of an apparatus (similar to that of Ref. 8) sketched in Fig. 6 with the light supplied through fiber optics. We have examined a number of different samples, made by either sputtering or closed space sublimation, having different back contacts, and areas from ~ 0.1 to 1 cm². Also, we have used different pressure applicators ranging from that covering almost the entire contact area to pogo-pins acting on local spots. All the examined cells showed qualitatively similar strong piezo-response, illustrated in Figs. 7 and 8 for the illumination of about 0.01 sun. In all

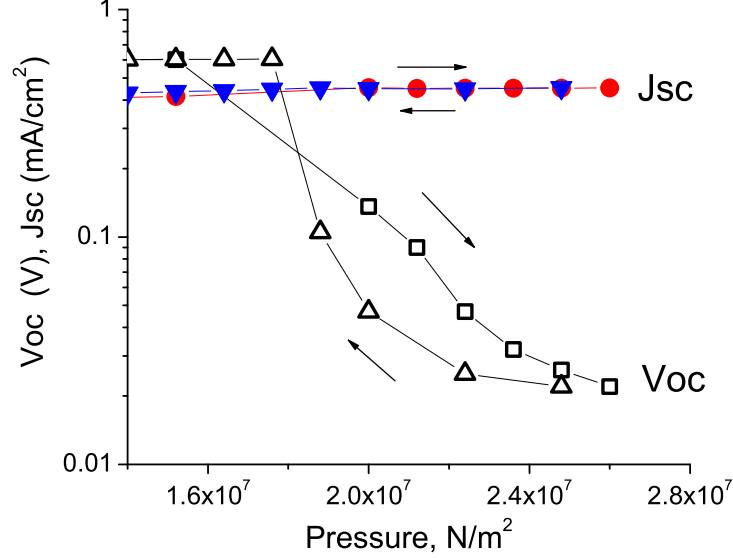


FIG. 7: Open circuit voltage (V_{OC}) and short circuit current (J_{SC}) of the CdTe/CdS solar cell versus pressure. Arrows show the directions of pressure change.

cases the effect was stronger for the case of small area applicators (pogo-pins), pointing at the pressure (and not the force) as a primary factor. The effect was found to start at higher pressures when the light intensity increased towards one sun, however retaining the amplitude from the original to almost zero V_{OC} .

The observed changes appeared fully reversible allowing multiple cycling back and forth, although with a considerable hysteresis for some of the parameters, such as V_{OC} . From the current-voltage (J/V) curves corresponding to different pressures, we have extracted the standard set of PV parameters: V_{OC} , short-circuit current J_{SC} , shunt resistance R_{SH} , and series resistance R_S . J_{SC} appeared the least sensitive showing $\lesssim 30\%$ changes attributable to pressure induced shift in the absorption edge [11] or other factors insignificant in what follows. As plotted against each other (Fig. 8) the above PV parameters showed almost no hysteresis, pointing to a well defined electronic structure corresponding to each particular pressure. The measured derivative $dV_{OC}/dP \sim 3 \cdot 10^{-8} \text{ Vm}^2/\text{N}$ is consistent with that estimated from Eq. (1) with $d_{33} \approx 10^{-11} \text{ C/N}$ [3], corresponding to the pressure along the c axis.

We were not able to explain our results within the framework of the 'standard' p-n junction model of Fig. 9 (a). Our interpretation is based on the metal-insulator-semiconductor (MIS) model of CdTe PV [13] where CdS plays the role of insulator (Fig. 9 (b); on different grounds, a CdS related potential barrier was suggested in Ref. 14). We assume the barrier height linear in pressure, consistent with Eq. (1), $V_B = V_{B0} - \alpha P$, $\alpha = d_{33}/C_0$, and the current-voltage characteristic

$$J = J_0 \{ \exp[q(V - JR_S)/kT] - 1 \} - J_L \quad (2)$$

with $J_0 \propto \exp(-V_B/kT)$ where all the parameters have their standard meaning and the saturation current is described in the temperature activation regime (assuming tunneling

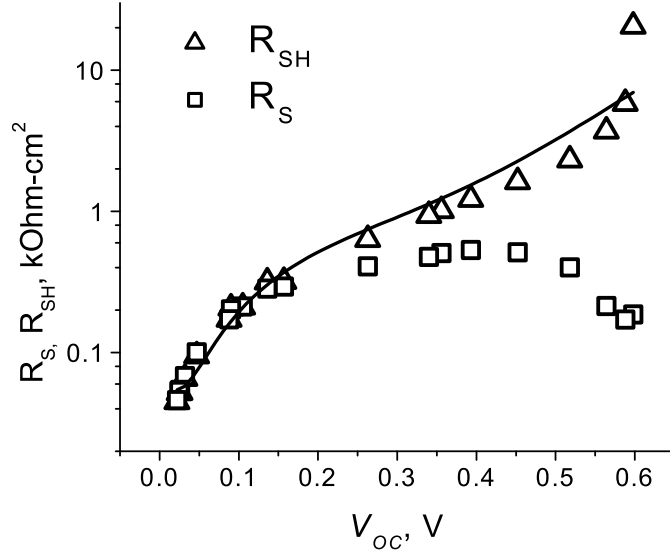


FIG. 8: Shunt resistance (R_{SH}) and series resistance (R_S) vs. device V_{OC} driven by the external pressure. The dependencies include both the pressure up and down sweep data points showing almost no hysteresis in this format. The curve shows a fit of R_{SH} by Eq. (3) where R_S is given by the data.

would not qualitatively change our conclusions). This yields $V_{OC}(P) = V_{OC}(0) - \alpha P$ and

$$R_{SH} \approx R_S + (kT/qJ_L) \exp[q(V_{OC} - J_L R_S)/kT] \quad (3)$$

consistent with the data (see the fit in Fig. 8). We do not discuss here the pressure dependence of R_S that can include a contribution from both the CdS related barrier and the back barrier (beyond the present framework).

Since the charge carrier concentration in CdS increases under illumination, the piezo-effects should weaken due to screening. This screening however can be highly nonlinear when determined by localized electric charges. In particular, our explanation of the observed hysteresis and persisting V_{OC} at P below a certain threshold P_{th} , takes into account electron traps strongly interacting with the piezo-induced charges and having long recharging times. P_{th} should create the electric potential capable of recharging such traps whose energies are of the order of V_{OC} . The condition that the piezo-voltage of Eq. (1), $V_j \sim V_{OC}(0)$ predicts P_{th} logarithmic in J_L and light intensity, which agrees with our data in the range of $\sim 0.01 - 1$ sun. The pyroelectric effect in CdS film [5] can be another source of P_{th} and hysteresis.

The band diagram in Fig. 9 (b) is consistent with the above observations and explains the following facts. (1) Piezo-effect; (2) MIS nature of the device that allows the reach-through band bending in CdTe caused by a properly chosen 'metal' layer on the other side of CdS [13, 15]; (3) buffer layers of certain morphology (for example, sputtered) strongly increasing V_{OC} (due to benign lateral strain in CdS) while other chemically and electrically

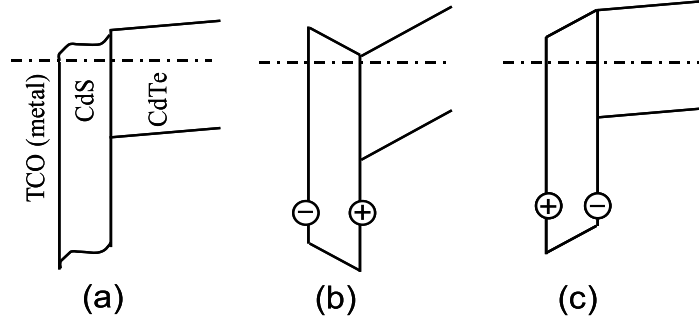


FIG. 9: Suggested band diagrams of CdTe/CdS PV. (a) p-n structure with n-type CdS and p-type CdTe. (b) MIS structure with insulating CdS where the electric field opposes that in CdTe. + and - mark the piezo-electric charges. (c) MIS diagram with CdS field capable of collecting the charge carriers. Dot-dashed lines show the Fermi level. For definiteness, the conduction band offset is set to zero; assigning it a finite value [12] would not affect the conclusions of this work.

equivalent layers (such as CVD) do not cause this effect [13, 15]. (4) Effects of Cu doping (due to Cu induced compensation, stress [7] and related piezo-voltage); (5) absence of carrier collection from CdS [1]; (6) dark JVs laying flat in the forward-bias region ('lay-downs') and light and dark JV crossover [16] (as a consequence of the potential barrier decrease under illumination); (7) negative quantum efficiency under the blue illumination for devices with thick CdS [17] (due to the opposite electric field orientation in CdS);

The above predicts a possibility of carrier collection from CdS by reversing the electric field in it (Fig. 9 (c)), possibly through CdS doping gradients. This gain in J_{SC} can be a trade-off situation with V_{OC} decreasing due to a weaker band bending in CdTe, as seen from the comparison of (b) and (c) in Fig. 9. Proper interfacial states could remedy the loss in V_{OC} by forming dipole layers (in combination with the piezo-charges), which may be another venue in device engineering.

Finally, we note that, because of the piezo-PV coupling, the diagram in Fig. 9 (b) represents a structure with energetically favorable grain orientation. Indeed, because they are electric dipoles, the grains in CdS will align themselves against the 'external' field generated by the photovoltaic effect; this orientation leads to the polarity of Fig. 9 (b) (which micro-structure correlates with predominantly S terminated CdS interface tangent to the TCO). In the case of CdTe PV, the alignment is likely to occur in the course of high-temperature CdCl₂ treatment, the technological step known to affect the grain morphology, but whose mechanism is not well understood [18]. This predicts that conducting the CdCl₂ treatment (or similar high temperature treatments) under illumination and/or external field will affect the device parameters.

The above results call upon further work on piezo-PV. Its experimental extension should include setups utilizing lateral stress, varying light spectra and intensity, and verifications of predicted practical recipes. A related theoretical study will concentrate on simulations of

piezo-related band diagrams, corresponding JV curves, and the thermodynamics of piezo-PV coupling.

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- [1] W. N. Shafarman and L. Stolt, in *Handbook of Photovoltaic Science and Engineering*, p. 567, Edited by A. Lique and S. Hegedus, Wiley 2003; B. E. McCandless and J. R. Sites, *ibid.*, p. 617.
 - [2] A. Carbonne and P. Mazzetti, Phys. Rev. B **51**, 13261 (1995); S. Hegedus, D. Ryan, K. Dobson, B. McCandless and D. Desai, in *Compound Semiconductor Photovoltaics*, B9.5.1, Materials Research Society Symposium Proceedings (2005), Vol. 763; D. Azulay, O. Millo, S. Silbert, I. Balberg, N. Naghavi, Appl. Phys. Lett. **86**, 212102 (2005).
 - [3] D. Berlincourt, H. Jaffer, and L. R. Shiozawa, Phys. Rev., **129**, 1009 (1963).
 - [4] F. A. Pizzarello, J. Appl. Phys. **38**, 1752 (1967);
 - [5] J. D. Zook and S. T. Liu, J. Appl. Phys. **49**, 4604 (1978).
 - [6] A. Fisher, Z. Feng, E. Bykov, G. Contreras-Puente, A. Compaan, F. Castillo-Alavarado, J. Avendano, and A. Mason, Appl. Phys. Lett. **70**, 3239 (1997).
 - [7] M. Paulraje, S. Ramkumar, K. P. Varkey, K. P. Vijayakumar, C. S. Kartha, K. G. M. Nair, Phys. Stat. Sol. (a), **202**, 425 (2005).
 - [8] M. S. Bennett and J. J. Kramer, J. Appl. Phys. **54** 7159 (1983).
 - [9] IEEE standard on piezoelectricity, in *Piezoelectricity*, Editors C. Z. Rozen, B. V. Hiremath, and R. Newnham, AIP, New York, 1992.
 - [10] B. E. McCandless, Materials Research Society Symposium Proceedings (2005), Vol. 865 *Thin-Film Compound Semiconductor Photovoltaics*, F6.1
 - [11] A. L. Edwards and H. G. Drickamer, Phys. Rev., **122**, 1149 (1961).
 - [12] M. Gloeckler, A. L. Fahrenbruch, and J. R. Sites, *Proceedings of the 3rd World Conference on Photovoltaic Energy Conversion*, Osaka, Japan, 11-18 May 2003, p. 2P-D52.
 - [13] Y. Roussillon, D. Giolando, D. Shvydka, A. D. Compaan, and V. G. Karpov, Appl. Phys. Lett. **84**, 616 (2004).
 - [14] G. Agostinelli, D.L. Botzner and M. Burgelman, *Proceedings 29th IEEE Photovoltaic Specialists Conference*, New Orleans, LA, 18 - 22 May 2002 IEEE, New York, 2002, p. 744.
 - [15] C. Ferekides, private communication; see: www.nrel.gov

/ncpv/thin_film/docs/DevPhys – Ferekides.ppt.

- [16] B. Tetali, V. Viswanathan, D. L. Morel and C. S. Ferekides, *Proceedings 29th IEEE Photovoltaic Specialists Conference*, New Orleans, LA, 18 - 22 May 2002 IEEE, New York, 2002, p. 600; T. J. McMahon and A. L. Fahrenbruch, *Proceedings of the 26th IEEE Photovoltaic Specialists Conference* Anaheim, September 29 - October 3, 1997, p. 539
- [17] S. Hegedus, private communication and *National CdTe R&D Team Meeting Minutes*, Editors P. V. Meyers and H. S. Ullal, NREL Golden, CO, January 27-28 (2000), Appendix 12.
- [18] R. H. Bube, *Photovoltaic Materials*, Imperial College Press, London 1998.